Comparison of plasma and piranha cleaning for surface preparation of gold (Au) prior to alkane thiol monolayer deposition using grazing incidence IR spectroscopy and microscopy

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Two of the most common gold (Au) surface preparation methods, plasma cleaning and chemical cleaning with acid piranha solution, were compared for the self-assembly of octadecanethiol (ODT) using grazing incidence FT-IR spectroscopy and microscopy. This work demonstrates that it is possible to observe signal from a thiol monolayer on gold using a low end commercial IR-Microscope, that thiol monolayers on gold exhibit some inhomogeneity on a microscopic scale (20-30 µm resolution), and that the two pretreatment methods do not give identical results. Plasma cleaning appears to yield somewhat more upright monolayers with less inhomogeneity than piranha cleaning.

1. Introduction

This work was undertaken to determine if a recently obtained IR-microscope was adequately sensitive to take spectra of self-assembled monolayers in the specular reflection mode. We were interested in investigating the homogeneity of metal-alkyl coupled monolayers [1] and phosphonic acid based monolayers, we have been studying. The well studied octadecane thiol on gold (Au) system was chosen to test the instrument. Two of the most common gold pretreatments, plasma cleaning [2-5] and piranha cleaning [6-10], were used. This work demonstrates that it is possible to observe signal from a thiol monolayer on gold using a low end commercial IR-Microscope, that high quality thiol monolayers on gold exhibit some inhomogeneity on a microscopic scale, and that the two pretreatment methods do not give equivalent results.

Self-assembled monolayers (SAMs) of thiols on Au substrates have been of considerable interest during the last two decades [11-13] for their potential nano-scale molecular applications. [6,14] The mechanical properties [6] and growth kinetics [6,16-19] of such layers have been extensively studied. A limited number of studies have addressed the homogeneity [20,21] of the SAMs and the effects of substrate preparation on the quality of the SAMs. [22-25]

Homogeneity has been tested using chemical etching to locate pinhole defects in SAMs, where etching of the Au substrate occurred. This work indicated that the number of defects can be low. [20] Infrared spectra of thin strips (~1.2 mm wide) across thiol SAMs suggest that the monolayers are homogeneous on the scale of a millimeter. [21] The spatially

resolved (resolution 20-30 μ m) infrared spectra reported here indicate that on a finer scale these monolayers are not homogeneous.

The oxidative state of the substrate surface has been shown to significantly influence the quality of the SAM packing for thiol SAMs terminated with polar functional groups, but not for methyl terminated SAMs. [22] Pre-existing surface contaminants are also a factor for the conformational order of the SAM. [6] Some report good results using gold substrates immediately after deposition in an evaporator or sputterer [23], but this is impractical for many laboratories. In many cases (including ours) the available deposition system is known to produce significant hydrocarbon contamination of the surface. The two most common surface preparation methods are chemical cleaning with an acid piranha solution [6-10] and plasma cleaning. [2-5] An acid piranha solution is a strong oxidant, and is believed to effectively remove any pre-existing moisture or organic substances from the Au surface. [26] Plasma cleaning converts organic contaminants on the surface to CO, CO₂, CH₄ and H₂O by exposing them to ions and radicals in a plasma, which is usually formed from air. [4] The UV/O₃ cleaning process appears to be similar to plasma cleaning. [4,23,24]Work by H. Ron et al. [23] showed that both plasma and piranha cleaning lead to metastable gold oxides on the surface, but only the oxide produced by plasma cleaning was easily reduced to gold on exposure to ethanol. Some of the oxide can be trapped under monolayers formed in ethanol solutions. [24] Ideally, these two cleaning techniques achieve the same level of surface cleanliness and adsorption of alkanethiol, but results presented in this work suggest that plasma cleaning may produce slightly cleaner surfaces and better final monolayers.

Grazing incidence reflection FT-IR spectroscopy was used to compare the monolayers, while FT-IR reflection microscopy was used to observe variations with position on the surface. The grazing incidence spectra imply that the plasma cleaned substrates develop more upright monolayers. However, there is no spectroscopic evidence of differences in average order between the two cleaning methods. For both cleaning methods, the adsorption of the alkanethiol varies from one place to another when observed microscopically. However, plasma cleaned surfaces exhibit less variation versus position.

2. Experimental Details

2.1 Substrate cleaning

Laser quality polished glass substrates (manufactured by ESCO) were pre-cleaned by rinsing with doubly filtered 18 M Ω deionized water, air drying and then plasma-cleaning for 2 minutes (PDC32G by Harrick Scientific Corporation). Substrates that were to be exposed to an acid piranha solution were primed with a 10 nm chromium layer by the manufacturer. Once pre-cleaned, glass substrates were immediately sputter-coated with gold (Au ~1000 Å) in an argon backfilled chamber (Vacuum Desk II by Denton). One set of Au coated substrates was plasma-cleaned for 10 minutes, using 10.5 watts to the RF coil (8-12 MHz modulation frequency) in 100 mTorr of room air, followed by 20 minutes in 200 proof stirred ethanol (Pharmco). The substrates was immersed in an acid piranha solution for 20 minutes followed by rising with 18 M Ω deionized water. The acid piranha solution was a

3:1 mixture of 18 M sulfuric acid (Fisher Scientific Corp.) and 30% hydrogen peroxide (Fisher Scientific Corp.). Each substrate was rinsed with 200 proof ethanol and was air dried with the filtered dry air used to purge the FT-IR before exposing it to the alkanethiol solution for monolayer growth.

2.2 Self-assembled monolayer (SAM) deposition

Au coated slides were immersed in 1.0 mM octadecanethiol (ODT, Aldrich, 98%) in 200 proof ethanol for 24 hours for the first measurement and 48 hours for the second. The same procedure was also used for 1.0 mM ODT in n-heptane.

2.3 Contact angle measurements

A 10 μ L, 18 M Ω water droplet was placed on the ODT treated surface, and advancing and receding contact angles were measured prior to the spectroscopic measurements. A video camera attached to a computer was used to collect movies of the drop on the horizontal surface as water was added and removed. The images were analyzed using NIHImage 1.61.

2.4 Spectroscopy

All spectra were collected using a Nicolet Nexus 670 FT-IR equipped with an MCT detector and controlled by Nicolet Omnic software. Large-area FT-IR spectra (grazing incidence reflectance) were obtained at a resolution of 4 cm⁻¹, and 1024 scans were averaged for each spectrum. No polarizer was used and the angle of incidence of the light was about 73°. The FT-IR chamber was purged with dry air provided by a Whatman FT-IR purge gas

generator. Spatially resolved FT-IR spectra were obtained using an IR microscope (InspectIR Plus by Nicolet) with an MCT detector. The samples were mounted in an optical holder on the microscope stage that physically indexed the sample surface to the same orientation each time. The spectral resolution was 2 cm^{-1} , and 1024 scans were averaged for each spectrum. Surface micrographs were taken of each location where an IR spectrum was obtained. The spectroscopically sampled spot size was experimentally measured by putting scotch tape on a glass slide with different sized gaps between the pieces of tape. The microns per pixel on the image was calibrated using the scale on the translation stage. This microns per pixel was then used to measure the size of the gaps between the tape. Spectra were taken in progressively smaller gaps until peaks associated with the tape were observed. This yields an estimate of the spot size of about 20 μ m in diameter, which is slightly less than the specification of 30-35 μ m.

2.5 Atomic force microscopy to compare sample surface area

Contact mode AFM images were collected on plasma cleaned and piranha cleaned gold surfaces, using a Park Scientific CP probe AFM and tips with a radius of curvature of 200 Å. Although visually the piranha cleaned samples appeared more pitted, for all scan sizes the measured surface areas of the samples were within less than 1% of each other. The surface area was calculated directly from the AFM image by estimating the area of the surface within each square defined by four neighboring pixels as the sum of two triangles.

3. Results and Discussion

3.1 Contact angles

Contact angles after 24 hour incubation in ODT/ethanol averaged 107 degrees advancing, 99 degrees receding for plasma cleaned substrates and 109 advancing, 103 degrees receding for piranha cleaned substrates. Uncertainties in these angles based on scatter of multiple measurements on single samples is ± 3 degrees. Both cleaning methods produced very hydrophobic surfaces with small hysteresis and essentially identical contact angles.

3.2 Large area grazing incidence spectra

Figure 1 shows large area grazing incidence FT-IR spectra of some typical surfaces. Both plasma and piranha cleaned substrates exhibit characteristic monolayer absorptions near 2960, 2920, 2880 and 2850 cm⁻¹, [11] assigned to the modes CH₃ asymmetric, v_a -CH₃, CH₂ asymmetric, v_a -CH₂, CH₃ symmetric, v_s -CH₃, and CH₂ symmetric, v_s -CH₂, respectively. The bottom two pairs of spectra were obtained under the same conditions as the top two except that n-heptane was used as the incubating solvent for ODT deposition on Au. No change was observed in ethanol solvent after 24 hours. Signals from samples incubated in nheptane for 24 hours were generally smaller than those incubated in ethanol, but increased to approximately the same after 48 hours. Samples prepared using either cleaning method yielded peak absorbances at ~2918 cm⁻¹ (v_a -CH₂) and ~2850 cm⁻¹ (v_s -CH₂); indicating that the self-assembled ODT monolayer forms in a predominantly ordered conformation. [27] Additionally, these spectra are consistent with those reported by others for well ordered monolayers of octadecanethiol on gold. [23,24,28,29]

In both solvents the integrated area of the v_s -CH₂ peak was observed to be larger in the piranha cleaned cases. Although the integrated area of the v_a -CH₂ peak was about the same or smaller in the piranha cleaned cases, it is believed to be an artifact of using piranha cleaned references, which have more CH₂ containing residues after cleaning than plasma cleaned references. This can be seen in the spectrum in the middle (Fig. 1(iii)) showing a piranha cleaned reference sample referenced to the plasma cleaned reference sample. The large hump seen in the v_a -CH₂ region would reduce the area of the observed v_a -CH₂ peak in the piranha sample, as well as explain the dip on the high energy side of the peak, which was sometimes observed in spectra of monolayers on piranha cleaned substrates (Fig. 1(ii)). This suggests that just like the v_s -CH₂ peak the v_a -CH₂ peak is actually more intense on the piranha cleaned than the plasma cleaned samples. Relative surface area cannot explain the variations in intensity as our AFM experiments indicate there is no significant differences in surface area between substrates prepared by plasma and piranha cleaning. This intensity difference is believed to indicate that the piranha cleaned samples are covered with somewhat more tilted and slightly less densely packed monolayers. [8, 28, 30] Because the molecules are siting on a metal surface, where there can only be significant electric field strength normal to the surface, the observed strength of these bands is strongly dependent on the orientation of the transition dipole for the -CH₂- modes relative to the surface normal. [28, 30] Other papers describe detailed analyses of the tilt of the molecules, but a simple model suffices to explain the increase in intensity as the tilt of the chains increases, despite the simultaneous decrease in number of absorbers. The molecules are approximated as cylinders. The highest density on the surface is achieved when the molecules are standing upright. The surface area occupied by a single upright molecule is just the cross-section of the cylinder. As the cylinders tilt over the surface area occupied by each cylinder becomes an ellipse, with the narrow dimension equal to the diameter of the cylinder and the long dimension described by the equation:

$$\mathbf{d}_{\mathrm{l}} = \mathbf{d}_{\mathrm{c}}/\cos\alpha,\tag{1}$$

where d_l is the length of the long dimension, d_c is the length of the short dimension (the cylinder diameter) and α is the tilt angle of the cylinder (the angle between the surface normal and a side of the cylinder). The area (A) of the ellipse (occupied surface area) is: [31]

A =
$$(\pi/4)d_cd_l = (\pi/4)d_c^2/\cos\alpha.$$
 (2)

The number of molecules per unit area is inversely proportional to A. This implies that the number of molecules on the surface (N) is proportional to $\cos\alpha$. Cos α goes to zero as α varies between 0 and 90° which implies that the number of molecules on the surface drop as expected with increasing tilt of the molecular chains. Since light absorption is proportional to the number of absorbers it appears that the signal from the -CH₂- modes should drop. However, the transition dipoles for the -CH₂- modes are perpendicular to the chain axis. This means that when the chain is tilted they can have a projection on the surface normal, the axis with the electric field from the incident light. The exact relationships are:

$$\mu_{a,z} = \mu_a \sin\beta \sin\alpha \tag{3}$$

$$\mu_{s,z} = \mu_s \cos\beta \sin\alpha, \qquad (4)$$

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where μ_a = the assymetric transition moment, μ_s = the symmetric transition moment, α = the tilt angle and β = the twist (angle of rotation of the symmetric transition moment out of the plane of the tilt). This is simply the dot product or scalar projection of the two transition moments on the surface normal. [32] Since the twist is determined by how the molecules pack together, the twist is not expected to change much as the molecules change tilt by small amounts. Thus we are only concerned with the effect of the tilt. The absorbance strength is proportional to the square of the transition dipole along the surface normal multiplied by the number of molecules. Thus for both of these transitions the absorbance intensity (I) is proportional to:

$$I \propto (\mu \sin \alpha)^2 \cos \alpha , \qquad (5)$$

where $\mu = \mu_a \sin\beta$ or $\mu_s \cos\beta$. [30] Equation 5 shows that the intensity (I) reaches its maximum value at 54.7° of tilt. For these well ordered layers others have determined that the tilt, α , is about 30° and the twist, β , is about 53°. [29] Assuming the plasma and piranha cleaned samples have roughly the same surface area and the monolayer tilt angles are near those observed by others the increase in signal observed for the piranha cleaned substrates suggests fewer and more tilted molecules than on the plasma cleaned substrates. It is worth noting that tilts of more than 79° are not reasonable as the spacing between molecules would be as large as the molecules are long, at which point they would be expected to lay flat on the surface.

3.3 Spatially resolved spectra

Figure 2A is a composite picture of four different areas, (i) - (iv), of a plasma cleaned Au surface that was incubated in an ODT/ethanol solution for 24 hours. There are no visible differences among the four locations where IR light was focused to collect spectroscopic signals. Figure 2B shows the FTIR reflection signals that correspond to the locations shown in Figure 2A (i)-(iv). The slight oscillations in the baseline indicate slight differences in the orientation of the sample and reference or a variation in flatness between the two. At all four positions the v_a -CH₂ peak is observed. However, the intensity does vary. On certain samples (not shown) in some positions no peaks were observed. Note that these signals are just barely observable above the noise level. The typical focal area of the IR incident light is approximately 500 μ m² (20-25 μ m in diameter).

Four different areas of a piranha-cleaned surface after 24 hour incubation in ODT/ethanol are shown in Figure 3A(i)-(iv). Again, the four locations where IR light was focused appear the same. In this case the peak intensities vary significantly with position and in some cases are much larger than in Figure 2. So some regions are probably more tilted. Also some peaks are shifted from those observed in the large area spectra (Fig. 1), suggesting significant variation in the environment experienced by the monolayer molecules. The same variations were observed on the samples incubated in ODT/n-heptane.

3.4 Statistical analysis of spatially resolved spectra

The data was also analyzed statistically to confirm that the differences seen among spectra versus position were significant compared to the uncertainty in the data. In order to present a larger data set the statistical analysis shown is one performed on a different set of samples than the ones presented in figures 1-3. On each sample four positions were identified by their coordinates using the microscope translation stage. Spectra were taken at each point one right after the other. There was roughly 20 minutes between the beginning of spectral collection at one point and the next. The rotation was repeated until at least three separate spectra had been taken at each point. Each spectrum had a linear baseline subtracted from it to adjust for instrument drift. The line was determined by linear least squares fitting to the data in the region of 2800 to 3000 cm⁻¹. The standard deviation among spectra at each particular position was calculated. The deviation at each wavelength for all of the positions on substrates prepared using both piranha and plasma cleaning is shown as dots in figure 4. These dots represent the reproducibility of spectra at a single position. Note that most of the dots are at deviations of less than 20 μ Abs. Thus at a single position spectra are very reproducible. The standard deviation over all the positions on a single sample was also calculated. This is shown in figure 4 for a sample prepared using plasma cleaning as a solid line.

The deviations versus position on the sample prepared by piranha cleaning are much larger than the deviations found at a single position. Even the smallest deviations are similar to the largest deviations seen at a single position. This suggests significant differences in the surface from position to position when the sample is prepared by piranha cleaning. The energy of the peaks in the deviations versus spot on the sample suggest some of the contributors to this variation. The peaks at about 2950, 2920 and 2842 cm⁻¹ are bands associated with C-H motions, suggesting significant variation in the coverage and orientation of the ODT monolayer versus position on the sample. The large band near 2950 cm⁻¹ is

associated with the CH₃ asymmetric stretch, suggesting that the terminal methyl group orientation varies the most versus position. This would be expected if some regions are less tightly packed, leading to a wider range of tilt angles and thus terminal CH₃ orientations.

The deviations versus position on the sample prepared by plasma cleaning shows significant sharp peaks in the 2950 to 3000 cm⁻¹ range. These bands are methane (CH₄) bands, indicating that small amounts of methane occasionally drift through the lab (the microscope stage is not purged). There are some other bands that <u>may</u> be statistically significant near 2854 cm⁻¹ and 2920 cm⁻¹ which would be associated with motions of the $-CH_2$ - groups. Thus there may be variations versus position in the orientation and coverage of the ODT monolayer on this plasma cleaned surface. However, these differences are smaller than observed on the piranha cleaned surfaces.

These statistical results confirm the variation seen by visually comparing spectra versus position within the same sample. Monolayers grown on surfaces prepared by piranha cleaning appear to vary more versus position than those grown on plasma cleaned surfaces. However, weak peaks associated with C-H vibrations are seen in the statistical analysis of plasma cleaned surfaces suggesting that there may be variations versus position that are on the order of the noise level in the spectra.

These results imply that the self-assembled monolayers are not uniform at the microscopic level. This contrasts with previous work where infrared spectra of thin strips (~1.2 mm wide) across thiol SAMs were taken using a planar array detector and a grating to provide spectral resolution. Those results showed small variations in spectra between lines

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and suggest that the monolayers were homogeneous on the scale of a millimeter. [21] Based on the results reported here those small variations may be indicative of inhomogeneity. Similar spectra of thin strips were also reported for octadecyltrichlorosilane and npropyltrichlorosilane monolayers on glass. [33, 34]

The spectroscopic selection rules on a metal surface provide a possible explanation for why spectra of small areas are necessary to see the evidence of inhomogeneity. Since the surface is a conductor the incident IR light cannot produce an electric field in the plane of This means that only vibrations with transition dipole components the surface. perpendicular to the surface can absorb infrared radiation. Well ordered alkane thiol surfaces have all trans -CH₂- chains tilted about 30° from the surface normal and twisted so that the backbone zig-zag is about 53° out of the plane of the tilt. [28-30] The strongest peak usually observed is associated with the -CH₂- asymmetric stretches which have transition dipoles perpendicular to the chain axis. Based on the simple model for signal intensity explained above, one can see that large area spectra will contain bigger contributions from molecules with tilts closer to 54.7°. This means that large area spectra will selectively sample well ordered but tilted molecules on the surface. If some areas have very upright molecules they may not contribute significantly to the large area spectra. Likewise, if the alkane tails are tilted beyond 54.7° they will be underrepresented in the large area spectra. In addition molecules that are very tilted are probably less ordered, because they do not have much tail overlap, and thus fewer van der Waals interactions to induce order. This means the twist angle may vary and there are likely to be more gauche defects in the chain further increasing number of -CH₂- stretch transition dipoles that are parallel to the surface and

cannot contribute to infrared absorption. This means that, except for undersampling of very upright regions, ordered regions will give larger signals for the same number of C-H bonds. Thus most of the signal seen in large area spectra will come from ordered regions. If a region that is mostly disordered or very upright is sampled in a small area spectrum, a different and lower intensity spectrum could be observed. Even if this disordered region made up a significant fraction of the surface it would only produce small perturbations on a large area spectrum of the sample.

Previous work on the effects of gold oxide on the growth of SAMs suggest that residual oxides can affect the quality of the monolayer formed. Thus it is possible that residual oxide on the surfaces may account for some or all of the observed microscopic variation in the monolayers. The same studies also indicated that oxides formed by piranha cleaning are harder to remove, which is consistent with the larger microscopic variation observed for piranha cleaned samples. [22-24]

4. Conclusions

Adsorption of octadecanethiol (ODT) on Au surfaces prepared using different cleaning methods were spectroscopically compared using large area and microscopic area reflection FT-IR. Both cleaning methods appear to produce very good coverage of ODT. Heterogeneous coverage was observed when the IR microscope was used. Grazing incidence FT-IR spectra suggest that plasma cleaned substrates develop more upright monolayers than piranha cleaned substrates. This work combined with the work of Ron *et al.* [24] and Tsai *et al.* [22] suggest that the best method for preparing Au for thiol adsorption is

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to use plasma cleaning followed by 20 minutes in stirred 100% ethanol and then transfer the substrate directly to an ethanol solution of the thiols for deposition.

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Figure 1: Comparison of FT-IR spectra of plasma-cleaned surfaces and acid piranha cleaned surfaces. (i) Plasma-cleaned substrate incubated in ODT/ethanol for 24 hours. (ii) Acid piranha-cleaned substrate incubated in ODT/ethanol for 24 hours. (iii) Negative logarithm of the ratio of the FT-IR signal from the plasma cleaned substrate and acid piranha cleaned substrate, -log(acid piranha/plasma). (iv) Plasma cleaned substrate incubated in ODT/n-heptane for 24 hours. (v) Acid piranha cleaned substrate incubated in ODT/n-heptane for 24 hours. Each spectrum is based on 1024 scans, including backgrounds. The resolution was 4 cm⁻¹.



Figure 2: (A: top) Surface images of a plasma cleaned substrate at 4 different locations. The substrate was incubated in ODT/ethanol solution for 24 hours. Each image frame is about 100 μ m wide. The circles represent the spectroscopically sampled spot, experimentally estimated at 20 μ m in diameter. (B: bottom) FT-IR spectra on the corresponding surface at positions (i)-(iv) obtained from IR microscope. Each spectrum is based on 1024 scans. The resolution was 2 cm⁻¹.



Figure 3: (A: top) Surface images of acid piranha cleaned substrate at 4 different locations. The substrate was incubated in ODT/ethanol solution for 24 hours. Each image frame is about 100 μ m wide. The circles represent the spectroscopically sampled spot, experimentally estimated at 20 μ m in diameter. (B: bottom) FT-IR spectra on the corresponding surface at positions (i)-(iv) obtained from IR microscope. Each spectrum is based on 1024 scans. The resolution was 2 cm⁻¹.



Figure 4: Standard deviation of signal. Small square dots are the deviations observed when sampling the same location multiple times. More than one location is included in the square dot data. The curves are the deviations observed when comparing multiple locations.

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